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(54) Formation acidising with foam

(57) A method of treating a subterranean formation penetrated by a well-bore comprising injecting into the formation a gelled, substantially unfoamed fluid as a pad fluid and thereafter injecting a foamed acid into the formation so that at least a portion of the formation is dissolved. The gelled, substantially unfoamed fluid is preferably sodium chloride saturated brine gelled with guar gum or hydroxypropyl guar.

SPECIFICATION

Well stimulation method using foamed acid

5 The present invention relates to a method of stimulating a subterranean formation penetrated by a well-bore by injecting a foamed acid into the formation. 5

It is generally known to use foamed acid to treat subterranean formations penetrated by a wellbore. Representative of prior art which teach foamed acids for such use are Plummer et al., U.S. 3,100,528, which also teaches a cushion of inert gas which may precede the foamed acid; Crawford et al., 15 *Journal of Petroleum Technology* 237 (March, 1963), which teaches a foamed acid treatment using carbon dioxide; 10 Neill et al., SPE Paper No. 738 (Oct. 6-9, 1963), which also teaches acidizing using carbon dioxide; Foshee et al., U.S. 3,323,593, which teaches compositions useful for fracturing and/or acidizing comprising foamed emulsions; Petty et al., U.S. 3,358,763, which teaches foamed acid treatments where nitrogen is added to the acid as a liquid, whereupon it vaporizes to form a foam; Jacobs et al., U.S. 3,330,346, 15 which is specifically directed to foams using a particular class of foaming agents but which teaches such foams may be used in acidizing; Anderson et al., U.S. 3,612,179, which teaches forming a foamed acid in situ by injecting in sequence, acid, an aqueous foaming agent, and a gas, and thereafter to inject another slug of acid; and Blauer et al., U.S. 3,937,283, which teaches optimum foam quality parameters.

Other prior art includes Plummer et al., U.S. 3,980,136, which is directed primarily to fracturing with 20 foam including a partial bleedback step, but which suggests that the fracturing foam may contain acid to stabilize clays; and Hutchinson et al., U.S. 3,463,231, and 3,572,440 which teach foamed acids, but apparently for use in cleaning a wellbore.

Notwithstanding the considerable body of prior art relating to foamed acid treatments, such treatments — particularly when carried out at rates and pressures sufficient to initiate or extend a fracture in a 25 subterranean formation — have not proved as successful as might have been expected. Laboratory tests suggest that relatively high fluid loss may be the reason. Although the present invention is not to be limited as to any particular theory as to why fluid loss was relatively high in prior art foamed acid systems, it appears to be due to a combination of factors such as, for example, breaking of the foam upon reaction of the acid with the formation resulting in high calcium ion levels, loss of surfactant on the formation, or 30 loss of inert gas altering the foam quality to a point where the foam is no longer stable. Fluid loss of the foamed acid upon contact with the formation is significantly reduced according to the present invention.

According to the present invention there is provided a method of treating a subterranean formation penetrated by a wellbore, which method comprises the steps of injecting into the formation a gelled, substantially unfoamed fluid as a pad fluid, and thereafter injecting a foamed acid into the formation so 35 that at least a portion of the formation is dissolved.

In the best mode presently contemplated for carrying out the present invention, from 7.0 to 30 weight percent, preferably about 15 weight percent, hydrochloric acid is used as the liquid portion of the foam. A suitable Mannich type inhibitor is also employed. Preferably, the foaming agent employed in the present invention is that disclosed in the commonly assigned application of James L. Thompson entitled "Foaming 40 and Silt Suspending Agent", Serial No. 281,964 filed July 4, 1977. The foaming agent there described is a blend of:

(A) at least one alkyltrimethylammonium chloride, wherein the alkyl chain length is from 8 to 18 carbon atoms and the mode alkyl chain length is 12 or 14 carbon atoms, and

(B) an amine oxide selected from bis (2-hydroxy-ethyl)cocoamine oxide, dimethylhexadecylamine oxide, 45 or dimethyl-hydrogenated tallowamine oxide, wherein component (A) and (B) are in a weight ratio to one another:

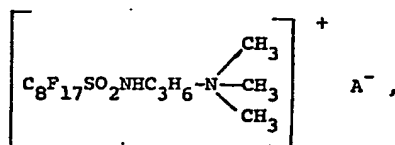
(i) from 45:55 to 85:15 when Component (A) is cocotrimethyl ammonium chloride and Component (B) is bis(2-hydroxyethyl) coco-amine oxide, and

(ii) from 40:60 to 95:5 when said Components (A) and (B) are selected so as to provide a combination 50 other than cocotrimethyl ammonium chloride and bis(2-hydroxyethyl) cocoamine oxide.

Most preferably the foaming agent employed is that described in application Serial No. 308,017, filed August 8, 1978, which, in addition to Components (A) and (B), also includes

(C) an adduct of trimethyl-1-heptanol plus seven moles of ethylene oxide; and

(D) a perfluorinated surfactant of the formula:



wherein A⁻ is Cl⁻, F⁻, I⁻ or Br⁻.

Components (C) and (D) are in a weight ratio to one another of from 1:1 to 40:1. Based on the weight of the liquid phase of the foam, the foam preferably contains Components (A) and (B) in a combined concentration of from 0.035 to 0.5 weight percent, most preferably 0.13 to 0.4 weight percent, and Components 65 (C) and (D) in a combined concentration of from 0.03 to 0.1 weight percent, preferably 0.037 to 0.07 weight

percent, provided as the 3:2 volume blend as described in application 308,017.

Sufficient inert gas is provided in combination with the acid to form a suitable quality foam. Preferably, the inert gas employed is carbon dioxide or nitrogen, and most preferably, a sufficient quantity is employed to give a Mitchell foam quality of from 0.55 to 0.85. Higher ratios of gas result in somewhat increased gas loss.

The gelled, substantially unfoamed fluid used as a pad may be gelled water, brine, or acid. Brine, preferably a sodium chloride saturated brine, is most preferred. By "substantially unfoamed" is meant containing insufficient gas to form a stable two phase comingled gas-liquid fluid mixture under the formation conditions. Ideally, the pad is unfoamed, but it is mechanically expedient to keep at least a small amount of gas flowing into the treatment line once the treatment has begun, and injection of a gel which is temporarily foamed at the earth's surface but which would not be predicted to remain foamed by the time it reaches the formation is considered within the scope of the present invention.

The thickening agents employable in the present invention include the natural, modified, and synthetic gums which are water soluble or dispersible and which do not precipitate in the presence of acid. Galactomannan gums and modified galactomannan gums are particularly useful as thickening agents in the present invention. A more detailed discussion of galactomannan gums suitable for use herein are described in Free, U.S. 3,974,077, at column 2, lines 18-49. Also ideally suited for use herein are the various water soluble or dispersible cellulose derivatives which are considered modified gums, such as alkylcelluloses, carboxyalkylcelluloses, hydroxyalkylcelluloses, and alkylhydroxyalkylcelluloses. Specific examples include, for example, carboxymethyl-, methyl-, hydroxypropyl-, hydroxypropyl-methyl-, hydroxyethyl-, or ethylhydroxyethylcellulose. Synthetic water soluble or dispersible gums such as certain vinyl polymers (i.e., those which do not precipitate in acid) and ethylene oxide polymers may also be employed as the thickening agent.

If desired, the gel may be a crosslinked system such as that taught by Chrisp, U.S. 3,301,723; Kern, U.S. 3,058,909; Free, U.S. 3,974,077 or Tinner et al., U.S. 3,888,312. However, uncrosslinked gels have generally proved satisfactory for purposes of the present invention. Also, in employing a crosslinked gel, care should be taken to select combinations of gelling agents and crosslinkers which do not form insoluble precipitates in the presence of acid.

When employing an uncrosslinked gel, the amount of thickening agent employed in the aqueous solution depends on the desired working viscosity of the solution. Aqueous solutions having viscosities ranging from 20 to 100 centipoise (cps) are desirable as measured with the Fann model 35 viscometer at 100 rpm at the temperature to which the fluid will be exposed. The exact amount of thickening agent to be employed in any particular aqueous solution will depend, for example, on the particular thickening agent employed and its viscosity building characteristics, the temperature of the fluid, the formation permeability, or the amount of time it is desired to have a maximum viscosity of the working temperature in the fluid. Generally from 20 to 100 pounds of the thickening agent per 1000 gallons of aqueous solution is employed (2.4 to 12 kg/m³). These parameters can be easily ascertained for any particular system by performing simple laboratory experiments.

If desired, conventional breakers — e.g., enzymes, persulfates, enediol compounds such as ascorbic acid as disclosed in the commonly assigned copending application of Clark et al., application Serial No. 302,820 filed May 5, 1978 — may also be employed in the pad fluid.

Preferably, the gelled pad fluid also contains a foaming agent. The foaming agents hereinabove described for the foamed acid may also be employed in the pad in generally the same proportions (calculated as a percent of the aqueous portion of the gel) is used in the foamed acid. The most preferred range for the total concentration of Components (A) and (B), however, is from 0.045 to 0.18 weight percent.

In carrying out the method of the present invention, the gelled pad and the foamed acid are injected into the formation in sequence. Both fluids may be injected at a matrix rate if desired. However, the advantages of the present invention are most apparent when the invention is practiced in the context of a fracture acidizing treatment, i.e., where at least one of, and usually both, the gelled pad and the foamed acid are injected at a rate sufficient to initiate or extend a fracture in the formation. In a fracture acidizing treatment, one or both of the gelled pad or foamed acid may contain a propping agent. Preferably, in either fracture acidizing or matrix acidizing treatments according to the present invention, the cycle of gelled pad fluid followed by foamed acid is repeated at least once and preferably a plurality of times.

If desired, the first stage of gelled pad fluid may be preceded by conventional acid, e.g., a stage of substantially foam-free and gelling agent-free 15 percent inhibited HCl, to initiate formation breakdown. A gelled pad preferably containing a surfactant blend of application Serial No. 308,017, filed August 8, 1978, may then be injected at a rate sufficient to initiate a fracture. Foamed acid and then alternating stages of gel and foamed acid may be injected to further propagate the fracture, and finally, the treatment may be concluded by displacing the final foamed acid stage with a suitable displacement fluid such as foamed brine.

The following examples and comparison runs further illustrate the practice of the present invention and its advantages over the prior art.

The following tests were carried out on 6-inch long limestone cores having a diameter of 1 inch. The cores were mounted vertically in a Hassler sleeve apparatus, and treatment fluids were injected upward through the core at a back pressure of 1000 psi. Unless otherwise noted, the foamed acid contained by

volume of liquid, about 0.4 percent a Mannich-type corrosion inhibitor and about 1.0 percent of the surfactant blend of said application Serial No. 281,964, namely a 75:25 volume blend of Arquad C-50 cocotrimethylammonium chloride solution and Aromox C/12 bis (2-hydroxyethyl) cocoamine oxide solution. Nitrogen was used as the inert gas for the foam.

5 Comparison Run 1

A core having a permeability to AP1 brine of 4.4 millidarcies (md) was purged with nitrogen. The core was then treated with foamed 28 percent hydrochloric acid having a Mitchell quality of 0.55. After 30 minutes, the nitrogen fluid loss, measured at 76°F and 1000 psi, was 51.6 ml.

Comparison Runs 2-4

10 Substantially identical tests were run using 0.65, 0.75, and 0.85 Mitchell quality foamed acid. Nitrogen loss test results were 38.1 ml, 44.5 ml (at 70°F), and 62.1 ml (at 70°F) respectively.

Comparison Run 5

15 In the same manner, on another core having a permeability to nitrogen of 4.4 md, the core was saturated with foamed brine prior to injection of the foamed acid. The acid concentration used was 15% HC1 which was injected as a 0.75 Mitchell quality foam. After 30 minutes, fluid loss was 12.6 ml nitrogen at 1000 psi and 64°F. This comparison run demonstrates that a foamed brine pad provides somewhat improved fluid loss control over that realized on a dry core.

Examples 1-4

20 In the same manner as in Comparison Runs 1-4, 28% foamed HC1 was injected as a 0.55, 0.65, 0.75, and 0.85 Mitchell quality foam into cores having a permeability to API brine of about 4.5. For each of these tests, however, the core was first saturated with tap water gelled with hydroxypropyl guar at a concentration of 40 lbs/1000 gallons of water (4.8 kg/m³). Nitrogen fluid loss after 36 minutes for each test was 1.2 ml (74°F), 0.9 ml (66°F), 2.4 ml (64°F), and 1.0 ml (72°F), demonstrating significant improvement over Comparison Runs 1-5. Moreover, the low fluid loss was realized over a relatively large range of foam

25 quality, making precise control of foam quality less critical.

Examples 5-8

Different gelling agents at a concentration of 40 lbs/1000 gallons of water were evaluated on cores having an API brine permeability in the range of 4 to 6 md according to the procedure of Example 1, i.e., using 0.55 quality foamed 28% HC1. After 36 minutes, nitrogen fluid loss results were as follows:

30	Gelling Agent	N ₂ Fluid Loss	30
	5. Hydroxypropyl guar	1.2 ml	
35	6. Guar Gum	0.5 ml	35
	7. Hydroxyethyl cellulose	2.1 ml	
	8. Carboxymethylhydroxyethyl cellulose	1.1 ml	

40 The foregoing results demonstrate that the aqueous gelling agent employed is not critical. Gelled kerosene was not effective, however. The kerosene apparently causes the foam to break. Nitrogen fluid loss using such a gelled kerosene pad was 49.6 ml after 36 minutes.

Examples 9-10

45 The following series of tests carried out at ambient temperatures using a hydroxypropyl guar pad and a 0.55 quality foamed 28% HC1, compares the effect of permeability and gelling agent concentration on fluid loss. In these tests, the pads were injected into the cores for 30 minutes at an average flow rate of 5.17 ml/min at 1000 psi. Results were as follows:

50	Gelling Agent concentration lb/1000 gal.	Core permeability, md	ml N ₂ 36 min.	50
	20	0.5	1.7	
	40	0.5	3.7	
55	20	4.6	8.9	55
	40	4.6	1.5	
60	60	about 100	28.4	60

65 For a 100 md core, the 28.4 ml of nitrogen loss is particularly remarkable. The foregoing data indicates lower viscosity gels may be preferable where the formation permeability is relatively low. Although the invention is not limited by theory, the data suggests the lower viscosity gels may be better able to penetrate the formation, thereby forming a deeper, i.e., thicker, wall of gel than can be achieved with the more viscous gels in formations having low permeability.

CLAIMS

1. A method of treating a subterranean formation penetrated by a wellbore, which method comprises the steps of injecting into the formation a gelled, substantially unfoamed fluid as a pad fluid, and thereafter injecting a foamed acid into the formation so that at least a portion of the formation is dissolved. 5
2. A method as claimed in claim 1, wherein at least the foamed acid is injected at a rate and pressure sufficient to initiate or extend a fracture in said formation.
3. A method as claimed in claim 1 or claim 2, wherein the injection sequence of gelled pad fluid followed by foamed acid is repeated at least once. 10
4. A method as claimed in any one of the preceding claims, wherein the gelled, substantially unfoamed fluid is gelled water, brine or acid. 10
5. A method as claimed in any one of the preceding claims, wherein the pad fluid is gelled with guar gum or hydroxypropyl guar.
6. A method as claimed in any one of the preceding claims, wherein the gelled pad fluid and/or the foamed acid contains a propping agent, and the propping agent containing step is injected at a sufficient rate and pressure to initiate or extend a fracture in the formation. 15
7. A method as claimed in any one of the preceding claims, wherein each of the pad fluid and the foamed acid contains a foaming agent.
8. A method as claimed in claim 7, wherein the foaming agent comprises a blend of: 20
- (A) at least one alkyltrimethylammonium chloride, wherein the alkyl chain length is from 8 to 18 carbon atoms and
- (B) an amine oxide selected from the group consisting of bis (2-hydroxyethyl) cocoamine oxide, dimethyl-hexadecylamine oxide, and dimethyl-hydrogenated tallowamine oxide, wherein Component (A) and Component (B) are in a weight ratio to one another of 25
- (i) from 45:55 to 85:15 when Component (A) is cocotrimethyl ammonium chloride and Component (B) is bis (2-hydroxy-ethyl) cocoamine oxide, and
- (ii) from 40:60 to 95:5 when said Components (A) and (B) are selected so as to provide a combination other than cocotrimethyl ammonium chloride and bis (2-hydroxyethyl) cocoamine oxide.
9. A method as claimed in claim 8, wherein said foaming agent additionally includes: 30
- (C) an adduct of trimethyl-1-heptanol plus seven moles of ethylene oxide; and
- (D) a perfluorinated surfactant of the formula: 30
- $$\left[\text{C}_8\text{F}_{17}\text{SO}_2\text{NHC}_3\text{H}_6 - \text{N} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \right]^+ \text{A}^- ,$$
- wherein A^- is Cl^- , F^- , I^- or Br^- , wherein 35
- Components (C) and (D) are in a weight ratio to one another of from 1:1 to 40:1, and wherein each of the pad fluid and the foamed acid (by weight of liquid phase) contains Components (A) and (B) in a combined concentration of from 0.035 to 0.5 weight percent and Components (C) and (D) in a combined concentration of from 0.03 to 0.1 weight percent. 40
10. A method of treating a subterranean formation penetrated by a wellbore, which method comprises, as an initial step, injecting an aqueous, substantially foam-free and gelling agent-free acid into the formation, injecting as a pad fluid, a gelled, substantially unfoamed fluid containing a foaming agent at a rate and pressure sufficient to initiate a fracture in the formation, injecting a foamed acid at a rate and pressure sufficient to extend said fracture, and injecting at least one additional cycle of said gelled pad fluid followed by foamed acid at a rate and pressure sufficient to further extend said fracture. 45
11. A method as claimed in claim 10, wherein in a further step the foamed acid is displaced with foamed brine. 50
12. A method of treating a subterranean formation penetrated by a wellbore substantially as hereinbefore described in any one of Examples 1 to 10.